

Thermodynamic behaviour of two-dimensional vesicles revisited

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Abstract. - We study pressurised self-avoiding ring polymers in two dimensions using Monte Carlo simulations, scaling arguments and Flory-type theories, through models which generalise the model of Leibler, Singh and Fisher [Phys. Rev. Lett. **59**, 1989 (1987)]. We demonstrate the existence of a thermodynamic phase transition at a non-zero scaled pressure \tilde{p} , where $\tilde{p} = Np/4\pi$, with the number of monomers $N \rightarrow \infty$ and the pressure $p \rightarrow 0$, keeping \tilde{p} constant, in a class of such models. This transition is driven by bond energetics and can be either continuous or discontinuous. It can be interpreted as a shape transition in which the ring polymer takes the shape, above the critical pressure, of a regular N-gon whose sides scale smoothly with pressure, while staying unfaceted below this critical pressure. Away from these limits, we argue that the transition is replaced by a sharp crossover. The area, however, scales with N^2 for all positive p in all such models, consistent with earlier scaling theories.

Fluid vesicles in three dimensions exhibit diverse shapes. This diversity originates in the nontrivial ground state configurations exhibited by a simple curvature Hamiltonian for a closed surface as the enclosed volume and surface area are varied [1]. Not much is known about the behaviour of such a model system at non-zero temperature. However, equivalent models in one lower dimension should provide useful insights into behaviour in the experimentally relevant three-dimensional case [1, 2]. The simplest such model is that of a self-avoiding polymer ring whose enclosed area couples to a pressure difference term [2–5].

Leibler, Singh and Fisher (LSF) [2] studied such a pressurised polymer model, defining the ring in terms of tethered discs. The energetics of the model derived from a pressure term conjugated to the enclosed area. Monte Carlo simulations and a scaling analysis about zero pressure were used to demonstrate that the radius of gyration R_G and the averaged area A obeyed the scaling forms $R_G^2 \sim N^{2\nu} X(\tilde{p}N^{2\nu})$ and $A \sim N^{2\nu} Y(\tilde{p}N^{2\nu})$, where $\nu = 3/4$ exactly in $d = 2$ and $X(x)$ and $Y(x)$ are scaling functions of a single scaling variable x . The dimensionless measure of the pressure difference is $\tilde{p} = pa^2/k_B T$, where p is the pressure difference, a is the diameter of the disc and T is the temperature, with the appropriate scal-

ing variable defined as $x = \tilde{p}N^{3/2}$. In a scaling regime around $x \simeq 0$, data collapse for a range of system sizes was observed by LSF, with a $x = 0$ transition separating branched polymer behaviour, for $p < 0$, from a $p > 0$ regime governed by the statistics of self-avoiding walks.

The LSF scaling description applies for finite $pN^{3/2}$. At large (positive) pressures, it is reasonable to expect that $A \sim N^2$, with the expanded shape approaching a circle. However, extending LSF-type scaling arguments to the large pressure case yields $A \sim N^3$ for large pressures, assuming only that $pN \ll 1$ [6]. Any expanded regime with $A \sim N^2$ is thus *inaccessible* through an expansion about the LSF fixed point at $\tilde{p} = 0$. Related scaling arguments, based on a blob picture, have recently been presented for the case in which the scaled pressure $\tilde{p} = Np/4\pi$ is finite and non-zero for large N [6, 7]. These suggest that self-avoiding pressurised chains should swell smoothly as \tilde{p} is increased, ruling out a phase transition at nonzero \tilde{p} .

However, there are models for pressurised polymer rings which *do* exhibit a continuous pressurisation transition at non-zero \tilde{p} , (although these models allow for self-intersections) [9, 10]. Recent work on ring polymers with a pressure term conjugated to the algebraic (signed) area, obtains a continuous transition, between a collapsed phase with $\langle A \rangle \sim N$ and an expanded phase with $\langle A \rangle \sim N^2$

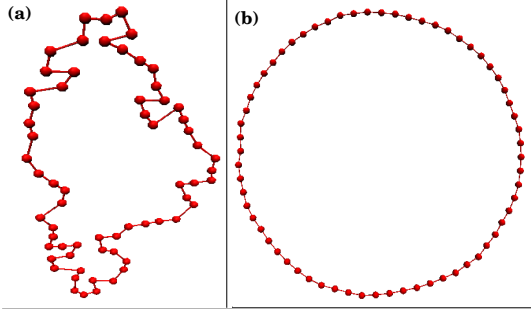


Fig. 1: Configurations of a self-avoiding pressurised polymer, with finite beads connected by quadratic springs of maximum extension R_0 (Model C). These figures illustrate sample configurations on either side of the transition; both for (a) $\tilde{p} < 1$ as well as for (b) $\tilde{p} > 1$, where \tilde{p} is the critical pressure.

[11,12]. The critical pressure, in a Flory-like theory, arises from the competition between an entropic R^2/N term, which favours more compact configurations, and a pressure term $-\tilde{p}R^2/N$, which favours expanded configurations. Such terms should also be present in theories for the self-avoiding case, supplemented by additional terms accounting for self-avoidance. Whether it is the true or the algebraic area which enters the Hamiltonian should also be irrelevant in the large pressure limit [11]. Thus, it is natural to ask whether the inclusion of self-avoidance suffices to destroy the non-zero \tilde{p} transition altogether or whether some trace of the singular behaviour at $\tilde{p} \sim 1$ in the self-intersecting case survives. If it does, this would indicate a hitherto unanticipated feature of such pressurised polymer ring models, with possible applications to the three-dimensional case.

This Letter demonstrates the existence of an unusual and somewhat subtle phase transition as \tilde{p} is increased across a critical value, in some models for pressurised, self-avoiding polymer rings. This transition can be either discontinuous or continuous, and separates a weakly inflated phase from a strongly inflated phase, in a sense we make precise below. The average area $\langle A \rangle$ scales as N^2 on both sides of the transition, in accord with earlier scaling arguments. Crucially, the *nature* of fluctuations changes across the transition point, with the ring expanding without feeling the effect of the maximum extension R_0 below the transition, while being constrained by R_0 at and above the critical pressure. Sample configurations below and above the transition are shown in Fig. 1. Interestingly, for models of the LSF type, such transitions appear to be absent in the thermodynamic limit, although their effects may be manifest in sharp crossovers.

We first summarise prior scaling arguments for this problem [6,7]. These use the blob picture, describing the polymer ring as a one-dimensional object fluctuating in two dimensions. In response to a relevant perturbation, the ring can be naturally decomposed into N/g blobs of g monomers each. A blob stores an average tensile en-

ergy equal to $k_B T = 1$, i.e. $\gamma\xi \sim 1$, where γ is the induced surface tension due to the perturbation and ξ is the blob size. At length scales smaller than the blob size ξ , the ring is unaffected by the perturbation, thus obeying $\xi \sim g^\nu$, where ν is the swelling exponent characterising the unperturbed manifold statistics. This implies that the surface tension scales as $\gamma \sim g^{-\nu}$. At length scales larger than ξ , the perturbation stretches the manifold; the total projected length of the chain is the product of the number of blobs and the projected length of each blob: $R \sim \left(\frac{N}{g}\right)\xi \sim N\gamma^{1/\nu-1}$. For pressurised rings, the surface tension and the pressure difference p are related via Laplace's Law, $\gamma/R \sim p$. The total projected length then scales as $R \sim N^{\frac{\nu}{2\nu-1}} p^{\frac{1-\nu}{2\nu-1}}$, while the average area scales as

$$\langle A \rangle \sim R^2 \sim N^2 (pN)^{\frac{2-2\nu}{2\nu-1}}, \quad (1)$$

with the surface tension given by $\gamma \sim pR \sim (pN)^{\frac{\nu}{2\nu-1}}$.

The above scaling argument, while justified for $pN \ll 1$, must be carefully examined for $pN \sim 1$, i.e. when the blob size and the microscopic cutoff are comparable. For the blob picture to be valid, the number of blobs should be larger than unity as well as less than N ; these conditions impose $N^{-2\nu} < p < N^{-1}$, or equivalently $pN < 1$.

The fact that such an analysis predicts a leading $\langle A \rangle \sim N^2$ behaviour, as is physically reasonable in the limit of large pressures, suggests that it is reasonable to assume that the ring should swell smoothly at *all* pressures, with the average area and surface tension described by the general scaling forms $\langle A \rangle = N^2 f_1(pN)$, $\gamma = f_2(pN)$ [7, 8]. This argument also accounts for the possibility of a phase transition in the self-intersecting case, since the exponent of the argument in the scaling functions above diverges at $\nu = 1/2$. Numerical simulations of a specific generalisation of the LSF model support the conjecture that no phase transitions occur upon varying \tilde{p} in this model and, by extension, in the general case [7].

Consider, however, Figs. 2(a) and (b). Both represent the variation of an appropriately normalised area as a function of a scaled pressure variable, in two different models of pressurised, self-avoiding polymer rings. As is apparent, the average area varies discontinuously in one model (Fig. 2(a)), whereas the other (Fig. 2(b)) appears to show a continuous transition.

Such behaviour is precluded by the scaling arguments discussed above, but it is easy to reason that the discrepancy originates in the extension of the blob picture to regimes where it is inapplicable. When $\tilde{p} \sim 1$, the energetics of the linkages connecting the monomers is probed [6]. Equivalently, the blob size reduces to the size of the monomer in this limit. Thus $\nu = 1$ since the ring is no longer fractal at or below this scale, and the exponent $(2 - 2\nu)/(2\nu - 1)$ in the expansion $\langle A \rangle \sim N^2 \left[(pN)^{\frac{2-2\nu}{2\nu-1}} \right]$ vanishes. Sub-leading corrections from perimeter contributions dependent on the detailed potential between particles constituting the ring, must then be accounted for.

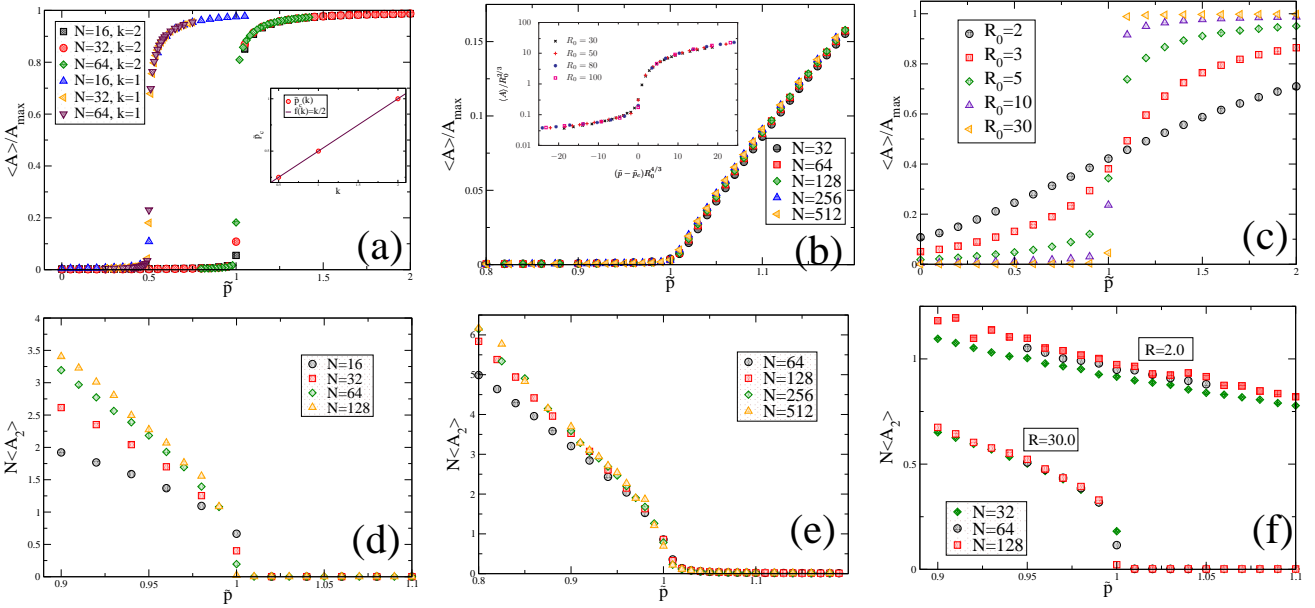


Fig. 2: Order parameter $\frac{\langle A \rangle}{A_{max}}$ for (a) [Model A], (b) [Model B] and (c) [Model C] and the scaled asphericity $N \langle A_2 \rangle$ for (d) [Model A], (e) [Model B] and (f) [Model C], illustrating their variation with the scaled pressure \tilde{p} . Model A, corresponding to (a) and (d), shows a sharp discontinuous jump in the order parameter, mirrored to a lesser extent in the asphericity. The inset to (a) shows the proportionality $\tilde{p}_c = k/2$ for Model A. For Model B, corresponding to (b) and (e), both quantities vary continuously across the transition. The inset in (b) shows collapse of the data for different R_0 , when $\tilde{p} - \tilde{p}_c$ and $\langle A \rangle$ are scaled as in Eq. 5. For Model C, as shown in (c) and (f), the transition can be sharp or non-existent depending on the ratio $\delta = a/R_0$. This behaviour can be seen both in the order parameter as well as the asphericity.

Models. — We define and study three models of pressurised self-avoiding ring polymers. The first, model A, consists of point particles connected by quadratic springs with a maximum extension of R_0 . The springs cannot intersect, thus enforcing self-avoidance. The potential between the particles takes the form

$$\begin{aligned} V(r) &= \frac{1}{2}kr^2, \quad r < R_0, \\ &= \infty, \quad r \geq R_0. \end{aligned} \quad (2)$$

The second, model B, again assumes point particles connected by springs with a maximum extension R_0 . However, the spring potential in this case is chosen to be of the Finitely Extensible Nonlinear Elastic (FENE) [13] type and is given by

$$\begin{aligned} V(r) &= -R_0^2 \ln \left(1 - \frac{r^2}{R_0^2} \right), \quad r < R_0, \\ &= \infty, \quad r \geq R_0 \end{aligned} \quad (3)$$

This form of the potential allows us to investigate the effect of a smooth divergence to infinity for r approaching R_0 , as opposed to the jump imposed in model A.

Our model C consists of monomers of finite diameter a connected by springs with a maximum length R_0 . Self-avoidance implies that no bead overlaps with another bead and that no bonds intersect each other. The spring

potential is a quadratic potential with a cutoff at the maximum bond length R_0 , as in model A. The relevant dimensionless parameter in this model is the ratio of the bead size to the maximum bond-length, $0 \leq \delta \equiv \frac{a}{R_0} < 1$. In the limit $\delta = 0$, we recover model A, whereas for $\delta = 1/1.8$, we obtain the analog of the LSF model, albeit with springs instead of tethers. The spring constant is chosen to be $k = 2$; results for other values of k are obtained by rescaling the pressure axis as $\tilde{p} \rightarrow 2\tilde{p}/k$ (see below).

Simulation Details and Measured Quantities. —

We have performed Monte-Carlo simulations of models A, B and C, combining both local (single bead) and non-local (multiple bead) moves [14]. The basic Monte Carlo move consists of choosing a bead at random and giving it a random displacement. Self-avoidance is ensured by checking that the random displacement does not lead to bond intersections or bead overlaps, if applicable [15]. The system is evolved typically for $\sim 4 \times 10^6$ Monte Carlo steps, with the relevant averages computed after discarding the first 10^6 steps for equilibration. We have also performed multi-particle moves involving the reflection of a group of n connected particles across the line joining the particles at the end. A variety of initial configurations are used to initiate the simulations. Defining bead positions on an underlying fine grid speeds up the simulations considerably.

We define the order parameter as the ratio of the average area to the maximum allowed area, $\Phi = A/A_{max}$ with

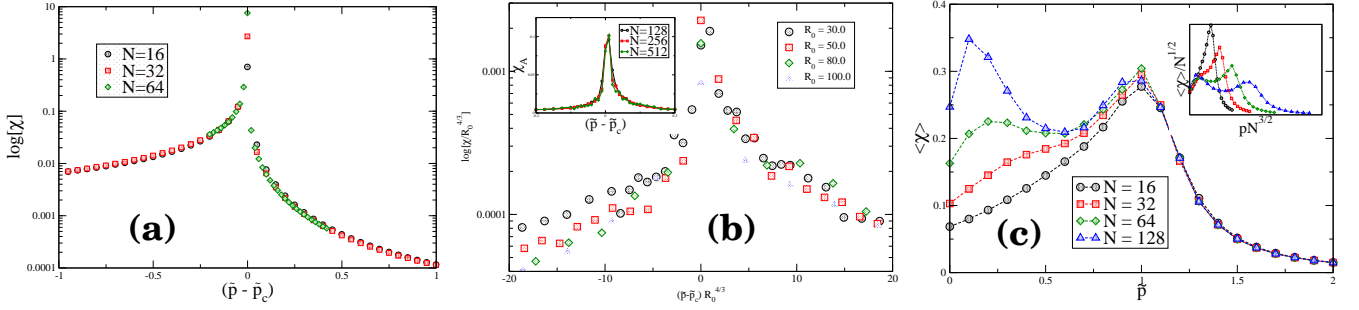


Fig. 3: Susceptibility plots for (a) model A, (b) model B and (c) model C. The first-order character of the area susceptibility of model A is shown in (a), with a delta-function singularity at the transition. In contrast, model B displays a power-law divergence of the susceptibility for different values of the bond length (R_0), shown in (b). The inset to (b) shows the susceptibility of model B for different values of the system size, which all collapse onto a single curve. The susceptibility for model C is shown for (c) for an intermediate value of the bond length ($R_0 = 3$). The plot shows two clear peaks, the second peak scaling with pN , and the first with $pN^{3/2}$ as shown in the inset to (c).

$A_{max} = \frac{1}{4}NR_0^2 \cot(\frac{\pi}{N})$, as appropriate to an N -gon of fixed side length R_0 . In the thermodynamic limit, defined as the double limit $N \rightarrow \infty$ and $R_0 \rightarrow \infty$, this order parameter should be zero for $\tilde{p} < \tilde{p}_c$ and nonzero above it.

The nature of the transition can be characterised through an appropriately defined susceptibility. We define the area susceptibility [11]

$$\chi = \frac{1}{\langle A \rangle} \frac{\partial \langle A \rangle}{\partial \tilde{p}}. \quad (4)$$

For a continuous transition, both the order parameter and susceptibility collapse around the critical point can be described by appropriately defined scaling functions

$$\Phi = R_0^{\theta_1} h_1[(\tilde{p} - \tilde{p}_c) R_0^{\theta_2}], \quad (5)$$

$$\chi = R_0^{\zeta_1} h_2[(\tilde{p} - \tilde{p}_c) R_0^{\zeta_2}]. \quad (6)$$

The instantaneous shape of the ring is characterised by the gyration tensor, defined as $T_{\alpha,\beta} = \frac{1}{N} \sum_{i=1}^N (X_{i,\alpha} - X_{CG,\alpha})(X_{i,\beta} - X_{CG,\beta})$, with $X_{CG,\alpha}$ denoting the α^{th} component of the centre of mass and $X_{i,\alpha}$ denoting the α^{th} component of the i^{th} particle. If the eigenvalues of this tensor are λ_1 and λ_2 , the radius of gyration $R_G^2 = \lambda_1 + \lambda_2$ and the asphericity A_2 is

$$A_2 = \left(\frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \right)^2. \quad (7)$$

This asphericity is 0 for a perfectly spherical shape and 1 for a rod-like shape.

Results. — We first discuss results for model A. The order parameter shows a first order jump for the system sizes shown, in which the number of monomers N ranging from 16 to 64, as well as for two different values of the spring constant k . At smaller k , the transition \tilde{p} shifts to smaller values; as shown in the inset, the critical scaled pressure equals $k/2$. There are no significant finite size effects in the data, with the data for $N = 16$ overlapping the

data for $N = 64$; this is also the case for much larger systems (not shown). Fig. 2(d) shows the asphericity across the transition; while A_2 vanishes asymptotically as N is increased both above and below the transition indicating that the asymptotic shape is a circle in both cases, there is a significant difference in the N -dependence of A_2 on both sides of the transition. The susceptibility (Fig. 3(a)) displays a classic first-order delta-function peak at the transition (note the logarithmic scale on the y-axis) with the peak height increasing with N .

The dependence of the critical pressure on k can be computed in the following way, relying on the assumption that fluctuations can be ignored for $\tilde{p} > \tilde{p}_c$: The pressurisation energy is $F_P = -4\pi^2 \tilde{p} \frac{R^2}{N}$. Adding the spring energy $F_S = \frac{N}{2} k (\frac{2\pi R}{N})^2 = 2\pi^2 k \frac{R^2}{N}$ to this gives $F_P + F_S = [-2\tilde{p} + k] \frac{R^2}{N}$ and thus a first-order transition at $\tilde{p}_c = k/2$, as seen in the data. The self-avoidance term will, of course, prevent collapse for $\tilde{p} < \tilde{p}_c$; a Flory theory discussed below indicates that $\langle A \rangle \sim N^2$ in this phase.

In contrast, order parameter results for model B (Fig. 2(b)), indicate a smooth increase from zero at the critical pressure value. The order parameter curves show no dependence on N but depends on R_0 above the transition. The asphericity (Fig. 2(d)) varies strongly with N below the transition, while the N -dependence essentially collapses above the transition. The susceptibility plots for model B are shown in Fig. 3(b). Data for different values of R_0 can be collapsed using Eq. 6, where the exponents $\zeta_1 \approx 1.33$ and $\zeta_2 \approx 1.33$ as shown in the inset to Fig. 2(b). The order parameter variation can also be collapsed using the form given by Eq. 5 with exponents given by $\theta_1 \approx 0.67$ and $\theta_2 \approx 1.33$. (The errors on these exponents are large, however, and conservative estimates of error bars are around ± 0.10 on each of the calculated exponents.) For $\tilde{p} < \tilde{p}_c$, we have $\frac{\langle A \rangle}{N^2} \sim (\tilde{p}_c - \tilde{p})^{-\theta_1/\theta_2}$, as illustrated in Fig. 4(a). Above the transition, the area order parameter can be calculated analytically (as shown in the next section) yielding, for $\tilde{p} > \tilde{p}_c$, $\frac{\langle A \rangle}{N^2} \sim (1 - 1/\tilde{p}) R_0^2$,

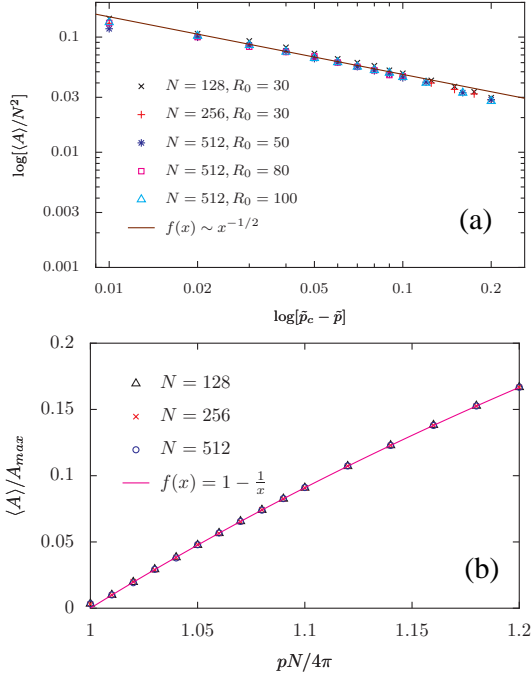


Fig. 4: (a) The divergence of area with pressure near the critical point for a range of system sizes and maximum bond lengths for model B; (b) The large pressure behaviour of the average area for model B. The data is shown for three system sizes $N = 128, 256, 512$ with $R_0 = 30.0$.

as illustrated in Fig. 4(b).

These results for self-avoiding rings with point particles then imply the following: If there is a finite maximum extension R_0 , then there is a transition such that $\lim_{R_0 \rightarrow \infty, N \rightarrow \infty} \frac{A}{A_{max}}$ is zero below the transition and non-zero above it. This transition separates a *weakly* expanded phase, in which the area scales as N^2 but is otherwise insensitive to the value of R_0 , from a *strongly* expanded phase, in which the area scales as $(NR_0)^2$. Depending on the form of the potential, the transition between these phases can either be discontinuous or continuous. The transition can also be characterised as a shape transition: below \tilde{p} , the asphericity A_2 is R_0 -independent for finite N while it decreases to zero with increasing R_0 above it.

To address the question of transitions in models of the LSF type, we now present our results for model C, where the monomers are now beads of a finite diameter a connected by springs with a maximum allowed extension R_0 . Order parameter plots for this model are shown in Fig. 2(c). For the smallest R_0 , the order parameter varies smoothly through the transition. As R_0 is increased, however, the variation becomes sharper, with what appears to be discontinuous behaviour of the order parameter at large R_0 . This behaviour is also apparent in the asphericity, shown for two values of R_0 in Fig. 2(f). For $R_0 = 2$ ($\delta = 1/2$), there is no transition, while for $R_0 = 30$ ($\delta = 1/30$), a sharp jump in the asphericity across the

transition is seen. The susceptibility plots for this model (Fig. 3(c)) show two distinct peaks, the first about $p = 0$ scaling as $pN^{3/2}$, and the second about $\tilde{p} = 1$, scaling as pN .

Thus either, (a) there is a critical value of δ below which there is no transition as a function of \tilde{p} and above which there is a discontinuous transition or, (b) there is no transition except in the limit of $\delta \rightarrow 0$ (model B), where a transition demonstrably exists. We conjecture that the second scenario is applicable, for the following reason: As $\tilde{p} \rightarrow \tilde{p}_c$, blob sizes becomes comparable to the microscopic cutoff. However, for finite beads, the monomer dimension bounds the blob size from below since fluctuations below this size cannot be resolved, giving the perimeter a finite width even in the limit of very large pressures. The smoothness assumption implicit in the blob-based scaling arguments should thus continue to hold, with both area and the surface tension varying non-singularly as p is increased. For models with non-vanishing δ , we therefore conjecture that there can only be a crossover, though possibly a sharp one, from the weakly to the strongly expanded phase. This is consistent with the observed absence of the transition at large pressures in LSF-like models [7].

Formally, a vesicle perimeter of mean length $L \sim 2\pi R$ undergoes transverse thermal wandering of a magnitude $u_{rms} \sim (2\pi k_B T/p)^{1/2}$ [6]. Note that u_{rms} is independent of N , validating a central assumption of the Flory theory presented later. Given $\gamma = pR$, the ratio of the intrinsic width ξ (blob size) to u_{rms} is $\frac{\xi}{u_{rms}} \sim (pN)^{\frac{\nu}{2\nu-1}} (\frac{p}{2\pi k_B T})^{1/2}$. Inserting $\nu = 3/4$, we obtain $\frac{\xi}{u_{rms}} \sim (\tilde{p})^{3/2} (p/2\pi k_B T)^{1/2}$. With $p \rightarrow 0, N \rightarrow \infty$, with $\tilde{p} = Np = \text{const}$, $\frac{u_{rms}}{\xi} \rightarrow \infty$; this conclusion holds true even if we assume $\nu \rightarrow 1$. Thus, any scale which bounds the blob size ξ from below, such as a bead dimension, should provide a smooth variation of $\langle A \rangle$ at all pressures.

Scaling Arguments. — A Landau formulation justifying the existence of a transition can be framed in terms of the competition between a surface free energy arising out of an effective tension term $\frac{N}{2}\sigma(\frac{2\pi R}{N})$ and the pressurisation term $-\tilde{p}\frac{R^2}{N}$. The expansion of the surface tension term yields terms of the form $\frac{R^2}{N}(a_0 + a_2\frac{R^2}{N^2} + a_4\frac{R^4}{N^4} \dots)$, where the lowest order contribution ($a_0 > 0$) is present even in the tethered case, from entropic elasticity. Combining terms of the same order yields a Landau free energy of the form $F_L \sim \alpha_0\frac{R^2}{N} + \alpha_1\frac{R^4}{N^3} \dots$, with the α_0 term changing sign at a critical value of the pressure. Such a Landau theory predicts an (area) order parameter exponent of 1 for the continuous case (model B), while comparing free energies on both sides of the transitions yields first order behaviour for model A, as seen. The nature of the $\tilde{p} < \tilde{p}_c$ phase requires consideration of the effects of self-avoidance.

A simple Flory-like theory, accounting for contributions from self-avoidance, pressurisation, entropy and bond stretching, provides a consistent explanation of the be-

haviour at all pressures. The stretching free energy is a function of the maximum bond length R_0 and the form of the potential between neighbouring monomers. For model B, (and, in fact, fairly generically) it is of the form $F_{\text{stretching}} \sim \frac{R^4}{R_0^2 N^3}$ [7]. Apart from a self-avoidance term F_{SA} , we may take over terms from the study of the pressurised self-intersecting ring, to get a Flory free energy $F \simeq F_{SA} + \frac{R^2}{N}(1 - \tilde{p}) + \frac{R^4}{R_0^2 N^3}$. To estimate F_{SA} , we assume that since the model is always in an expanded phase with $\langle A \rangle \sim N^2$, F_{SA} is well represented by small fixed-width fluctuations about the N-gon shape. The contribution to the free energy from self-avoidance is then approximated as $F_{SA} = N^2/R$ (as opposed to N^2/R^2 for a two dimensional self avoiding ring). Minimising this free energy yields the following predictions,

$$\langle A \rangle \sim \langle R^2 \rangle \sim \begin{cases} \frac{N^2}{(1-\tilde{p})^{2/3}}, & \tilde{p} < \tilde{p}_c \\ N^2 R_0^{4/5}, & \tilde{p} = \tilde{p}_c \\ N^2 R_0^2 (\tilde{p} - 1), & \tilde{p} > \tilde{p}_c \end{cases} \quad (8)$$

Note that $\langle A \rangle$ always scales as N^2 and is independent of R_0 below the transition. Above the transition, $\langle A \rangle \sim (\tilde{p} - 1)$, increasing linearly just above the transition, consistent with Fig. 2(b) and Landau-theory predictions. Thus, such a Flory-type scaling theory predicts the existence of a transition at a critical value of the scaled pressure. The exponents for the area scaling predicted using this Flory theory are $\theta_1 \approx 4/5$ and $\theta_2 = 6/5$, at the outside limit of the error bars of the values we obtain numerically for Model B (0.67 and 1.33). However, errors on these exponents in the simulations are substantial and the predictions of our Flory-type theory may possibly be correct.

The behaviour of the area above the transition can be computed analytically. In this regime, the shape of the polygon ring is simply a regular polygon and the free energy is simply the sum of the pressurisation energy and the spring energy. For a regular polygon of side a , the area is given by $A = \frac{1}{4}Na^2 \cot(\frac{\pi}{N})$, while $A_{\text{max}} = \frac{1}{4}NR_0^2 \cot(\frac{\pi}{N})$, where R_0 is the maximum allowed bond length. For Model B, the free energy can be written as, $F = -pA - NR_0^2 \ln(1 - \frac{A}{A_{\text{max}}})$. The average area is obtained from $\partial F / \partial A = 0$, giving $p = \frac{4 \tan(\pi/N)}{1 - \frac{\langle A \rangle}{A_{\text{max}}}}$. Defining $\tilde{p} = \frac{1}{4}p \cot(\frac{\pi}{N})$, we obtain $\tilde{p} = \frac{1}{1 - \frac{\langle A \rangle}{A_{\text{max}}}}$. Note that this definition for \tilde{p} is in fact the correct one, reducing to the usual $\tilde{p} = \frac{pN}{4\pi}$ for large system sizes. Thus

$$\frac{\langle A \rangle}{A_{\text{max}}} = 1 - \frac{1}{\tilde{p}}. \quad (9)$$

This relation predicts the behaviour of the area very accurately for large pressures and is consistent with numerical data extending almost up to the critical pressure for large R_0 , where it coincides with the prediction from Flory theory: $\langle A \rangle \sim N^2 R_0^2 (\tilde{p} - 1)$ to lowest order. This is shown in Fig. 4(b).

Conclusions. — We have studied the thermodynamics of several models which generalise the original model of LSF. We demonstrate the existence of a phase transition in an appropriately scaled, pressure-like quantity. This transition is best thought of as a shape transition, in which the polymer conformation and area scaling are independent of a parameter R_0 which sets the maximum bond size below the critical pressure, while depending strongly upon it above. The polymer ring is un-faceted below the transition and faceted in the form of an N-gon just above, swelling smoothly thereafter while retaining its faceted shape as the pressure is increased further above \tilde{p}_c . Such transitions can be discontinuous or continuous in the limit that the ratio of the bead size to the characteristic scale of bead separation vanishes. In the general limit, where this ratio is non-zero, we conjecture that no transition exists, a conclusion which should apply to models of the LSF type.

The possibility of a genuine phase transition in an appropriately scaled pressure variable in models for self-avoiding pressurised rings has not been raised before, although the presence of such a transition in the self-intersecting case has been settled decisively [11,12]. Simple Flory-type theories appear to give useful insights into the transition. A similar study for the three-dimensional case may yield important insights and would appear to be very worthwhile.

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